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ON THE ANALYSIS OF DYNAMIC BEHAVIOR  
OF HIGH POLYMERS

## Introduction

Extensive work has been published concerning the dynamic behavior of high polymers. In a paper by Bordoni, Nuovo, and Verdini (1) (BNV), which we will discuss at length in the present paper, many references can be found. BNV found the characteristic time of partial relaxation, in polymethyl methacrylate, to be an unphysically small value in the order of  $10^{-18}$  sec.; a value even smaller than the highest mechanical vibration period through a perfect periodic lattice (2). In this paper, we will propose a method to analyze the dynamic behavior. One of the results of this method shows that the characteristic time, based on the experimental data of these authors, is in fact only in the order of  $10^{-8}$  sec.

## Dissipation Function

In the partial relaxation of the chain motion in high polymers, the temperature dependence of the energy dissipation shows a broader peak than the peak obtained from the single relaxation time theory (3). Various expressions have been introduced to describe this broader peak (4), but we believe one important feature was not taken into account, that is, the symmetry of the dissipation peak in the  $1/T$  diagram. Elsewhere we have discussed the significance of the symmetrical and unsymmetrical dispersion (5), and a special dispersion function was proposed (6,7).

In an appropriate notation, the function becomes,

$$Q^{-1} = S \cos^{\beta} \lambda \sin \beta \lambda \quad (1)$$

where  $Q^{-1}$  is the coefficient of the energy dissipation;  $S$  has the meaning of modulus defect,  $\lambda = \cot^{-1} \pi f \tau_0$  with  $f$  as the vibration frequency and  $\tau_0$  as the characteristic relaxation time;  $\beta$  is an empirical parameter,  $0 \leq \beta \leq 1$ . The case  $\beta = 1$  reduces eq. (1) to a single relaxation time dispersion function.

## Analysis

In this section, we will analyze the dissipation data of polymethyl methacrylate of BNV. The numerical value discussed is from Figure 10 of their work.

Some useful graphs of eq. (1) have been given in Ref. 6. With appropriate modification, as indicated in that reference, additional numerical graphs to facilitate calculations can be found in the work of Davidson (8). Usually the left-half and right-half widths of the dissipation peaks are compared. In the present case, the left-dissipation value does not reach 0.5. Therefore, we will compare the widths at  $Q^{-1} Q_m^{-1} = 0.8$ . At this value, we find

$$\begin{aligned} \frac{W}{k} (T_m^{-1} - T^{-1}) &= +4.67 \text{ on the right} \\ &= -6.98 \text{ on the left} \end{aligned} \quad (2)$$

This relative left-excess of the absolute value of the widths can be well approximated by taking  $\beta$  closely to 0.3. However, we cannot obtain the absolute value of these widths unless we replace the value of  $W = 0.273$  of BNV by  $W' = aW$  with, of course,  $a \neq 1$ . From  $\beta = 0.3$ , we find  $a = 0.21$  gives a good quantitative fit as shown in Figure 1. In the same figure, we show a curve obtained from the Fuoss-Kirkwood function (9) with  $\gamma = 0.117$  as given by BNV. This Fuoss-Kirkwood curve represents the global broadening of the dissipation peak well; therefore it is an im-

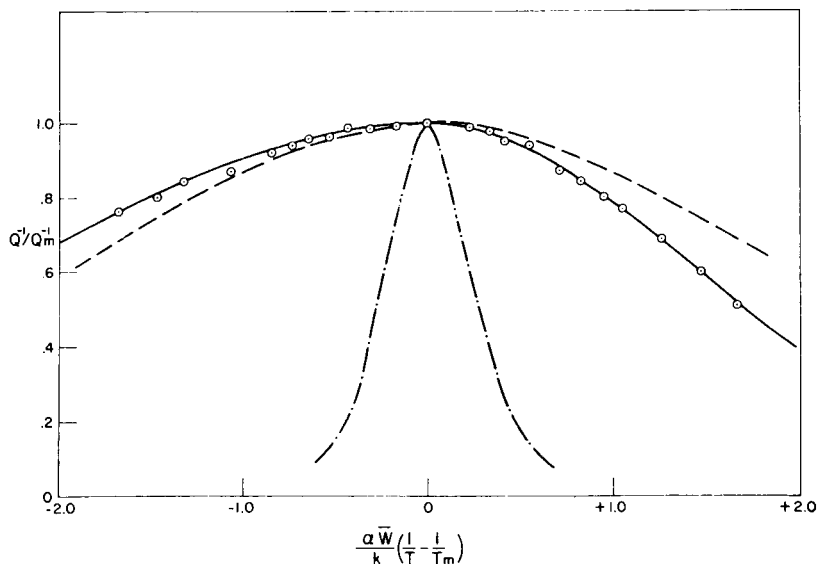


Fig. 1. Temperature dependence of the dissipation coefficient of the polymethyl methacrylate specimen 1(b) of Bordoni *et al* of Ref. 1. (⊙) experimental data; (—) Zeners dissipation curve; (---) Fuoss-Kirkwood function with  $\gamma = 0.117$  (from Table IV of Ref. 1); (-·-) present dissipation function.

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provement of the single relaxation time curve (also shown in Figure 1), but fails to reproduce the unsymmetry aspect.

The most drastic effect is on the value of the characteristic relaxation time. With  $W'$ , from the relation of BNV,

$$\tau_0 = \frac{1}{2\pi f_m} \exp \left[ -\frac{W'}{kT_m} \right] \quad (3)$$

Substituting the values of  $f_m = 12.88 \times 10^3$  c./sec. and  $T_m = 110.5^\circ\text{K.}$ ,

$$\tau_0 = 3.1 \times 10^{-8} \text{ sec.} \quad (4)$$

To be exact, neither  $\tau_0$  of eq. (4) nor  $\bar{\tau}_0$  of BNV has the significance of a "center of the spectrum." This center, which we understood to be the most probable distribution, is given by (6)

$$\tau = \tau_0 \cot \frac{\pi}{2(1 + \beta)} \quad (5)$$

with  $\beta = 0.3$ , and therefore

$$\tau = 1.2 \times 10^{-8} \text{ sec.} \quad (6)$$

This result is obtained in a natural way by invoking a consistent mathematical analysis.

In the case of Fuoss-Kirkwood dispersion, BNV gives the following relation for the modulus

$$S = (2/\gamma) Q_m^{-1} \quad (7)$$

Our corresponding expression is

$$S = 2Q_m^{-1} [\cos^1 + \beta \left[ \frac{\pi}{2(1 + \beta)} \right]] \quad (8)$$

Therefore, a similar interpretation of the temperature dependence of the characteristic time and the number of elementary processes is permissible in the present formalism.

#### References

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